

AD-A260 662



2

OFFICE OF NAVAL RESEARCH

GRANT # N00014-92-J-1629

R&T Code 4133037---01

Technical Report No. 1

NMR Studies of Ion Mobility and Association  
in Polyether-based Polymer Electrolytes

by

Steven G. Greenbaum

Prepared for Publication in

*Polymers for Advanced Technology - Special Issue on Ion Conductive Polymers*

Hunter College of CUNY  
Department of Physics  
New York, NY 10021

January 25, 1993

Accession For	
NTIS	CRA&I <input checked="" type="checkbox"/>
DTIC	TAB <input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

DTIC QUALITY INSPECTED 8

DTIC  
ELECTE  
FEB 11 1993  
S E D

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale:  
its distribution is unlimited.

93

2 10 1993

93-02547



REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 25 January 1993	3. REPORT TYPE AND DATES COVERED Interim Technical Report (4/92-		
4. TITLE AND SUBTITLE NMR STUDIES OF ION MOBILITY AND ASSOCIATION IN POLYETHER-BASED POLYMER ELECTROLYTES		5. FUNDING NUMBERS Grant number N00014-92-J-1629		
6. AUTHOR(S) Steven G. Greenbaum		R&T Code 4133037---01		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Physics Department, Hunter College of CUNY 695 Park Ave., New York, NY 10021		8. PERFORMING ORGANIZATION REPORT NUMBER 1		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research, Chemistry Division 800 N. Quincy Street, Arlington, VA 22217-5660		10. SPONSORING / MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES Accepted for publication in "Polymers for Advanced Technology" (special issue on Ion Conductive Polymers)				
12a. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release and sale; distribution unlimited		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words)  The results of several investigations of polyether-based polymer electrolytes by nuclear magnetic resonance (NMR) spectroscopy conducted in the author's laboratory and by other groups are reviewed. For both $^7\text{Li}$ and $^{23}\text{Na}$ NMR, the onset of motional line-narrowing occurs at about the glass transition, illustrating the importance of polymer segmental motion to ion transport. Examples of the ability of NMR to probe cation-anion interactions are discussed. These include chemical shift variations corresponding to different $\text{Li}^+$ environments and nuclear quadrupole coupling and relaxation behavior as a probe of $\text{Na}^+$ environment.				
14. SUBJECT TERMS Polymer electrolytes; lithium-7 and sodium-23 NMR; ionic and segmental mobility; ionic association		15. NUMBER OF PAGES 21		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT UL	

**NMR STUDIES OF ION MOBILITY AND ASSOCIATION IN POLYETHER-BASED  
POLYMER ELECTROLYTES**

Steven G. Greenbaum  
Department of Physics  
Hunter College of CUNY  
New York, NY 10021 USA

**Key Words:** Polymer Electrolytes;  $^7\text{Li}$  and  $^{23}\text{Na}$  NMR; ionic and polymer segmental mobility;  
cation-anion association

Received

**SPECIAL ISSUE ON ION CONDUCTIVE POLYMERS**

## ABSTRACT

The results of several investigations of polyether-based polymer electrolytes by nuclear magnetic resonance (NMR) spectroscopy conducted in the author's laboratory and by other groups are reviewed. For both  $^7\text{Li}$  and  $^{23}\text{Na}$  NMR, the onset of motional line-narrowing occurs at about the glass transition, illustrating the importance of polymer segmental motion to ion transport. Examples of the ability of NMR to probe cation-anion interactions are discussed. These include chemical shift variations corresponding to different  $\text{Li}^+$  environments and nuclear quadrupole coupling and relaxation behavior as a probe of  $\text{Na}^+$  environment.

## 1 INTRODUCTION

Solvent-free polymer electrolytes based on poly(ethylene oxide) (PEO) or other polyethers have been studied extensively in recent years. [1-3] Because the ion conducting phase is amorphous, structural information that could shed light on the ion transport mechanism is limited to essentially nearest neighbor coordination. Several experimental techniques, namely extended x-ray absorption fine structure (EXAFS), [4] vibrational (e.g. infrared and Raman) spectroscopy, [5] and nuclear magnetic resonance (NMR) are well-suited to probe the local environment of ions within the polymer complex. EXAFS is limited to relatively high-Z elements which, unfortunately, rules out studies of ionic environments in Li- and Na-containing polymer electrolytes. Although NMR is, of course, limited to magnetic nuclei, both  $^7\text{Li}$  and  $^{23}\text{Na}$  are very accessible due to their favorable nuclear properties (gyromagnetic ratio, natural abundance, etc.). NMR can also be utilized to probe dynamics of the polyether chains via  $^1\text{H}$  and  $^{13}\text{C}$  measurements and, in some cases, to study anion motion. An example of the latter involves the use of  $^{19}\text{F}$  NMR for appropriate anions (e.g.  $\text{BF}_4^-$  or  $\text{CF}_3\text{SO}_3^-$ ).

Although it is well established that ionic conduction depends critically on host polymer segmental motions occurring in the amorphous phase (for heterogeneous materials that also have a crystalline phase), further elucidation of the specific ion transport mechanism is complicated by the competition between cation-polyether segment and cation-anion interactions, where the latter are certainly expected to be significant in materials with salt concentrations (4 - 20 ether oxygens/cation) intended for most electrochemical applications. Vibrational spectroscopic techniques have yielded important results regarding the formation of ion pairs or higher multiplets under a variety of conditions such as salt concentration and temperature. [5] In cases that will be discussed in detail later, NMR measurements provide complementary information concerning ion association effects. An important point to be made when comparing results obtained at optical and radio frequencies is that the formation of an ion pair or cluster is apparently a dynamic process. In particular, exchange between "free" ions and ion multiplets may occur at a rate that is fast compared to NMR time-scales but slow compared to optical time-scales. Consequently, the two kinds of measurements would give different interpretations of ion association phenomena.

NMR measurements figure prominently in studies of molecular structure and dynamics. Although the most common use of NMR involves analytical measurements of organic molecules in solution, generally referred to as high resolution NMR, an extensive array of techniques and associated hardware exist for investigating solids. For example, cross-polarization and magic angle spinning (CPMAS) allow the acquisition of high resolution spectra in solids.[6] By virtue of chemical shift, nuclear dipolar or quadrupolar interactions, NMR is extremely sensitive to variations in short-range structural and bonding arrangements, which makes it such a valuable technique in studying polymeric or otherwise disordered materials. However in addition to structural information obtainable from spectra, the use of various pulse techniques facilitates the measurement of relaxation times which are of particular value in probing ionic or polymer segmental dynamics. For example, NMR has long been considered an important technique in studies and even initial screening of solid electrolytes.[7]. In some cases ionic self-diffusion coefficients can be measured directly by pulsed field gradient (pfg) methods.[8]

The basic theories and methodology of NMR can be found in several textbooks,[9] while additional review articles or texts provide descriptions of specialized applications or techniques. Among the latter are those already cited [6-8] as well as reviews on NMR applied specifically to polymer electrolytes.[10]. The following section contains a review and discussion of recent experimental results obtained in the author's laboratory and by other investigators as well. The review and discussion will focus primarily on issues directly related to ionic mobility and cation-anion interactions.

## **2 REVIEW OF EXPERIMENTAL RESULTS**

NMR measurements that shed light on the phase behavior of heterogeneous PEO-Li salt complexes were pioneered by Berthier and co-workers.[11] In addition to evaluating the relative fractions of crystalline and amorphous phases via linewidth and relaxation time differences of  $^7\text{Li}$  nuclei residing in the two phases, the NMR results provided some of the earliest evidence that ionic transport occurs only in the amorphous phase. That ion mobility is highly coupled to polymer segmental motion is convincingly demonstrated by the observation of motional NMR line-narrowing above the glass transition temperature ( $T_g$ ).

Though there are many examples of this in the literature,[10 and references therein] only several cases selected from investigations in our laboratory will be discussed here.

Before reviewing these cases we mention some important contributions from other groups concerning NMR studies of ion mobility via pfg techniques. As discussed in the Introduction, whereas linewidth and relaxation data can provide only a qualitative description of ionic diffusion, pfg measurements can yield ionic self-diffusion coefficients directly. Although the technique is limited to relatively fast diffusion coefficients ( $D \geq 10^{-12} \text{m}^2 \text{s}^{-1}$ ) and sufficiently long spin-lattice relaxation times ( $T_1 \geq 100 \text{ ms}$ ), pfg measurements are well-suited for measuring  $\text{Li}^+$  transport in polymer electrolytes. Through the use of  $^{19}\text{F}$  NMR and the commonly employed counterion  $\text{CF}_3\text{SO}_3^-$ , anion transport can be measured as well. These measurements were first applied to polymer electrolytes by Mali and co-workers [12] and later by Bhattacharja and co-workers [13]. An important conclusion of the latter study was that cation and anion mobilities are comparable, a result which has been verified by other "direct" techniques such as radiotracer diffusion [10(a)] or electrochemical transference number measurements. [14] It is now known that anion transference numbers can often be greater than 0.5.[2,3] Recently pfg measurements have been performed on low molecular weight analogues of PEO complexed with  $\text{LiCF}_3\text{SO}_3$ . [15] Deviations between measured and calculated (on the basis of the Nernst-Einstein relation and measured ionic diffusivity) conductivities were interpreted as evidence for short-lived ion-pairs, or at least strongly correlated cation and ion motions. However these deviations were only significant at low salt concentrations or high values of reduced temperature, leading to the conclusion that single-ion (both cations and anions) transport processes dominate the conductivity at high salt concentrations.[15]

Returning to the observation of motional line-narrowing as useful means of characterizing polymer electrolytes, a recent study [16] of polymer electrolytes based on composites of poly[bis((methoxy-ethoxy)ethoxy)phosphazene] (MEEP) and PEO or poly(propylene oxide) (PPO) complexed with lithium salts provides an illustration of the use of NMR in characterizing cation mobility in materials with complicated phase diagrams. Figure 1 displays the  $^7\text{Li}$  linewidths of seven samples as a function of temperature whose compositions (and  $T_g$ 's) are summarized in the figure (Fig.1 is taken from [16]). The most obvious feature of the temperature dependence is the onset of motional line-narrowing

corresponding to  $T_g$  of the respective samples. Samples with a relatively high PEO content also exhibit a discontinuity in linewidth as the material is heated above the melting point of PEO. That this discontinuity is not observed upon cooling reflects the slow recrystallization kinetics. This behavior is similar to that reported in earlier studies of PEO-salt complexes.[10] A third noteworthy feature of the data in Fig.1 is that the samples containing  $\text{LiBF}_4$  have  $^7\text{Li}$  rigid (low T) linewidths that are about 25% greater than those of the samples containing  $\text{LiClO}_4$ . It will be shown later, for other polymer electrolyte materials, that the origin of this additional broadening lies in the heteronuclear  $^7\text{Li} - ^{19}\text{F}$  dipolar interaction. Because nuclear dipole interactions fall off as the third power of the internuclear separation this provides a clear indication of close cation-anion proximity. We will discuss cation-anion interactions further following a review of selected  $^{23}\text{Na}$  NMR results.

$^{23}\text{Na}$  has many desirable properties as a probe of ion mobility and ion-ion interactions in polymer electrolytes. It, like  $^7\text{Li}$ , is a spin-3/2 nucleus and is therefore subject to nuclear electric quadrupole interactions which are a rich source of information regarding bonding configurations and motional processes. The magnitude of the  $^{23}\text{Na}$  quadrupole moment, relative to that of  $^7\text{Li}$ , generally allows a greater degree of distinguishability between different kinds of ionic environments. For example  $\text{Na}^+$  solvated by polyether oxygens yields a distinctly different NMR response than  $\text{Na}^+$  residing in ion clusters. Another, more subtle, advantage of  $^{23}\text{Na}$  NMR arises from the dynamics of the process by which the central  $\pm 1/2$  transition becomes averaged above  $T_g$ . [10(b)] In particular, there are three distinct features in the temperature dependence of the  $^{23}\text{Na}$  central transition linewidth that correspond to motional correlation times, as shown in Fig.2 (taken from [10(b)]). This is in contrast to the single correlation time given by the reciprocal of the angular Larmor frequency which is associated with the  $T_1$ -minimum in spin-lattice relaxation measurements. A disadvantage of  $^{23}\text{Na}$  is that spin-lattice relaxation times in the mobile phase are typically several hundred microseconds which precludes the use of pfg techniques. Temperature dependencies of the  $^{23}\text{Na}$  linewidth in a wide variety of polymer electrolytes are remarkably similar as shown in Fig.3. The data in Fig.3 correspond respectively to: (a) oxymethylene-linked amorphous PEO complexed with  $\text{NaCF}_3\text{SO}_3$  or  $\text{NaI}$ :[17] (b)  $\text{PPO}_8\text{NaX}$ , where X is I,  $\text{ClO}_4$ ,  $\text{SCN}$ ,  $\text{CF}_3\text{SO}_3$  and  $(\text{CF}_3\text{SO}_3)_{0.5}(\text{I})_{0.5}$ :[18] and (c) poly(monophenylsiloxane-co-ethylene oxide) complexed with



$\text{NaCF}_3\text{SO}_3$ . [19] As discussed in the case of  $^7\text{Li}$ , the most striking feature of the  $^{23}\text{Na}$  linewidth temperature dependence is the onset of motional line-narrowing in the vicinity of  $T_g$  which, for all of the samples represented in Fig.3, has been measured directly by DSC. The linewidth reaches a minimum value and then broadens with further increases in temperature. This behavior is the experimental manifestation of the calculated dynamics of central transition averaging (in half-integer spin systems) shown in Fig.2.[10(b),20]

The general shape of the linewidth vs.  $T$  curves of all Na-containing polymer electrolytes studied in our laboratory is roughly constant, although  $T_g$  varies from  $\sim 200$  K in siloxane-based materials [19] to 305 K in  $\text{PPO}_8\text{NaB}(\text{C}_6\text{H}_5)_4$ . [21]

Careful examination of the  $^{23}\text{Na}$  NMR signal often reveals two lineshape components, where only one of them is associated with mobile  $\text{Na}^+$  ions. This effect is most evident in high molecular weight PPC complexes. While PPO does not solvate ions as strongly as PEO, due to its lower dielectric constant (relative to PEO) and steric effects associated with the methyl group, [22] it is, for precisely this reason, an extremely useful host polymer for studying cation-anion interactions. In addition, the amorphous nature of PPO complexes frees them from the complications associated with heterogeneity in PEO complexes. Figure 4 shows two components of the total  $^{23}\text{Na}$  free induction decay (FID) of  $\text{PPO}_8\text{NaI}$  at 329 K [23]. The components are easily separable by their different  $T_1$ 's, the short  $T_1$  ( $\sim$ ms) component corresponding to mobile  $\text{Na}^+$  ions solvated by the polymer segments while the longer  $T_1$  (s) component is associated with immobile ion-clusters. [18,23] An important precaution that must be observed in such measurements is to use quartz rather than pyrex sample tubes because the latter contain sodium. In fact, even the external (to the rf coil) dewar of the variable-temperature probe can interfere with the "immobile" Na signal in cases where the integrated intensity of the immobile fraction is only a few percent of the total integrated signal. Nevertheless it has proven possible to observe changes in mobile/immobile ion ratios as a function of  $T$  in a manner analogous to the previously cited Raman measurements by Kakihana and coworkers. [5(c)] In most cases of the PPO-Na salt complexes studied, the mobile ion concentration exhibits a slow increase with increasing  $T$  and then a decrease, which often culminates in the salt precipitating out of the polymer. [17] Figure 5 displays the  $^{23}\text{Na}$  spectrum of  $\text{PPO}_8\text{NaClO}_4$  at 413 K (from [18]), which is approximately the temperature at which the salt precipitates out as measured by DSC. The

spectrum clearly exhibits separate components due to precipitated salt and  $\text{Na}^+$  ions remaining in the polymer complex. For comparison a partially saturated spectrum is also shown, illustrating the vastly different  $T_1$ 's of the two components.  $T_1$  values of precipitated salt are similar to, though somewhat longer (typically by a factor of  $\sim 2 - 3$ ) than, those of the immobile ion clusters corresponding to Fig.4.

Although the kinds of interactions observable by  $^{23}\text{Na}$  NMR are not generally as apparent with  $^7\text{Li}$  NMR (of course, one of the reasons for this may involve chemical factors that have nothing to do with NMR), there are some exceptions. An example of this is shown in Fig.6, which depicts the full and partially saturated  $^7\text{Li}$  spectra at elevated T (363 K) of a MEEP/PPO mixture complexed with  $\text{LiClO}_4$  (from [16]). X-ray diffraction has revealed that some of the  $\text{LiClO}_4$  comes out of the complex at elevated T, and the presence of the precipitated salt is manifested in the extra, easily saturable spectral component in Fig.6. Other kinds of  $\text{Li}^+$ -anion association that fall short of salt precipitation, i.e. ion pairing and clustering, are less visible spectroscopically than in their Na counterparts, mainly due to the large quadrupole interactions associated with the  $^{23}\text{Na}$  nucleus in a low symmetry environment. In particular,  $^{23}\text{Na}$  in a cubic crystalline salt experiences nearly zero quadrupole coupling (except for that associated with random crystal imperfections), while  $^{23}\text{Na}$  solvated by ether oxygens is characterized by very strong quadrupole interactions. [20] 21

The resulting contrast in both spectral appearance and relaxation behavior between Na in precipitated salt or ion clusters, and Na within the polymer segment environment is thus large. Different  $\text{Li}^+$  environments are often distinguishable only by relaxation behavior or, in some cases, by small chemical shift differences for which MAS techniques must be employed. Although no specific structural picture has been proposed, close proximity between  $\text{Li}^+$  and  $\text{BF}_4^-$  ions in  $\text{PEG}_n\text{LiBF}_4$  complexes (PEG = poly[ethylene glycol, and  $n = 9$  or 25] at low T (below  $T_g$ ) has been observed directly via the  $^7\text{Li} - ^{19}\text{F}$  dipole-dipole interaction. [24] Figure 7 [from 24] shows static low-T  $^7\text{Li}$  spectra of  $\text{PEG}_9\text{LiBF}_4$  which illustrate separately the effects of  $^1\text{H}$  and  $^{19}\text{F}$  decoupling. The proton decoupling yields a dramatic decrease in linewidth which is similar to that reported for poly(propylene glycol) (PPG) complexes by Chung and coworkers, [25] and demonstrates the strong dipolar coupling between  $^7\text{Li}$  and protons associated with the polyether segments. The  $^{19}\text{F}$  decoupling, while not as dramatic, does reduce the central portion of the linewidth by  $\sim 10\%$ , which is

approximately the difference in linewidth between these samples and similar materials containing  $\text{LiClO}_4$  instead of  $\text{LiBF}_4$ . Measurements on  $\text{PEG}_{25}\text{LiBF}_4$  also show these effects which indicate close cation-anion proximity (at low T) even in more dilute complexes.[23]

With regard to ion pair and cluster identification in Li-containing polymer electrolytes, O'Gara and coworkers have recently utilized CPMAS  $^6\text{Li}$  NMR, which appears to be a promising alternative to  $^7\text{Li}$  due to its greater chemical shift resolution.[26] In studies of  $\text{PEO}:\text{LiClO}_4$ , three distinct  $^6\text{Li}$  peaks were assigned to different kinds of dissociated  $\text{Li}^+$  ions while two additional peaks assigned to isolated ion pairs and larger clusters were distinguished on the basis of their  $^1\text{H}$  cross polarization responses.[26]

The question of what mechanism drives ion association and, in some cases, salt precipitation in polymer electrolytes remains controversial. Ratner and coworkers discuss an entropic mechanism which is related to volume differences between the polymer-salt complex and the polymer plus precipitated salt.[27] On the other hand, dielectric measurements of PPO coupled with salt precipitation trends among Na salts with different anions suggested that electrostatic considerations were important.[23] Although a more complete model for ion association and salt precipitation should almost certainly include both electrostatic and entropic considerations, measurements in our laboratory are currently underway which should provide some input into the latter factor. In particular, ion association in Na-salt PPG as a function of host polymer molecular weight are in progress. Additional information on ion association and salt precipitation may be forthcoming from hydrostatic pressure measurements. Pressure is an additional thermodynamic variable whose modest ( $\sim$ several kbar) application can yield large changes in ionic conductivity and NMR linewidths and relaxation times. Previous measurements have provided evidence of a conductivity activation volume that is consistent with strongly correlated motion of the ions and the polymer segments, and NMR linewidths suggest a shift in  $T_g$  of  $\sim 10 - 15$  K/kbar.[19,23] A study of the effect of hydrostatic pressure on ion association is also in progress.

## ACKNOWLEDGEMENTS

The contributions of long-time coworkers J.J. Fontanella, M.C. Wintersgill, K.J. Adamic and Y.S. Pak are gratefully acknowledged. Some of the work described herein was supported

by the U.S. Office of Naval Research and the PSC-CUNY Award Program.

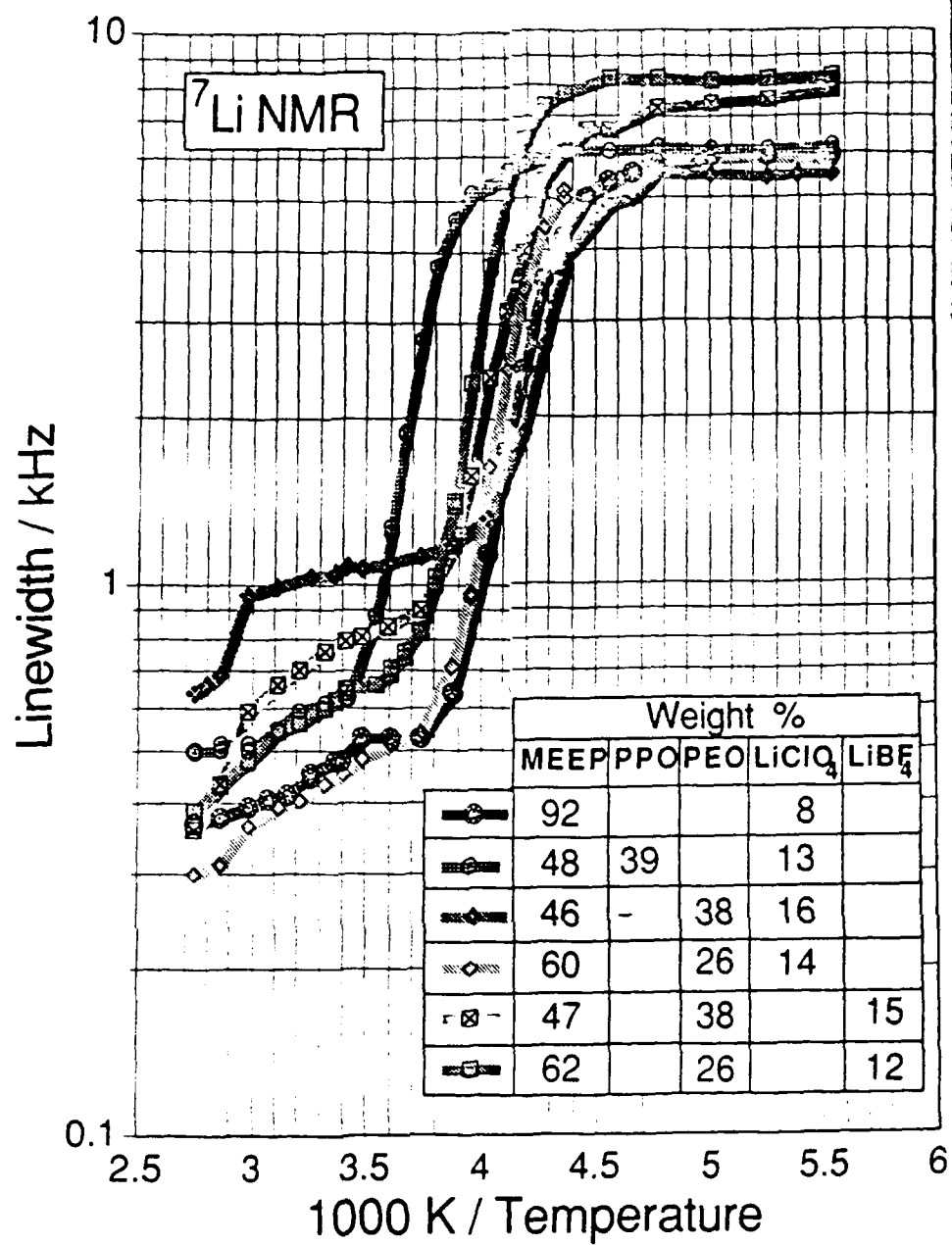
## REFERENCES

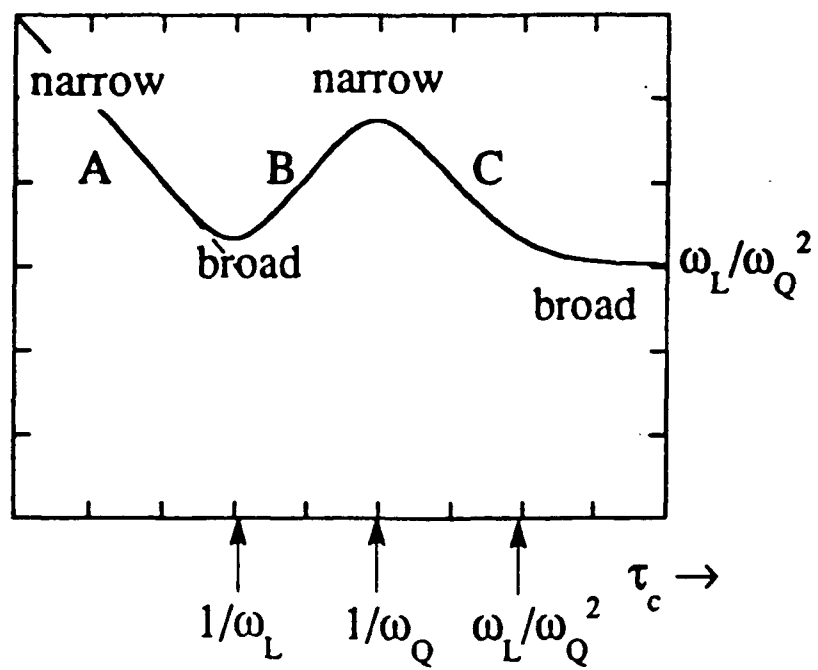
1. M.B. Armand, *Ann. Rev. Mat. Sci.* **16**, 245 (1986)
2. J.R. MacCallum and C.A. Vincent, editors: *Polymer Electrolyte Reviews 1&2*, Elsevier Applied Science, London and New York, 1987, 1989.
3. B. Scrosati, editor: *Second International Symposium on Polymer Electrolytes*, Elsevier Applied Science, London and New York, 1990.
4. K. Andrews, M.Cole, R.J. Latham, H.M. Williams and R.R. Dobson, *Solid State Ionics*, **28/30**, 929 (1988).
- 5.(a) R. Dupon, B.L. Papke, M.A. Ratner, D.H. Whitmore and D.F. Shriver, *Journal of the American Chemical Society* **104**, 6247 (1982). (b) D. Teeters and R. Frech, *Solid State Ionics* **18/19**, 271 (1986). (c) M. Kakihana, S. Schantz and L.M. Torell, *Journal of Chemical Physics* **92**, 6271 (1990).
6. C.A. Fyfe: *Solid State NMR for Chemists*, C.F.C. Press, Guelph, 1983.
7. D. Brinkmann: in T.A. Wheat, A. Ahmad and A. Kuriakose, editors. *Progress in Solid Electrolytes*, Canmet, Ottawa, 1983, p.1.
- 8.(a) E.O. Stejskal and J.E. Tanner, *Journal of Chemical Physics* **42**, 288 (1965). (b) R.E. Gordon, J.H. Strange and J.B.W. Webber, *Journal of Physics E* **11**, 1051 (1978).
- 9.(a) A. Abragam: *The Principles of Nuclear Magnetism*, Oxford University Press, 1961. (b) C.P. Slichter: *Principles of Magnetic Resonance*, 3<sup>rd</sup> edition, Springer-Verlag, Berlin, 1990. (c) E. Fukushima and S.B. Roeder: *Experimental Pulse NMR, A Nuts and Bolts Approach*, Addison-Wesley, Massachusetts, 1981.
- 10.(a) A.V. Chadwick, in Reference 2, vol.1, p.275 (1987). (b) S.G. Greenbaum, Y.S. Pak K.J. Adamic, M.C. Wintersgill and J.J. Fontanella: in G. Nazri, editor. *Materials Research Society Symposium Proceedings: Solid State Ionics II* **210**, 1991, p.237.
11. C. Berthier, W. Gorecki, M.B. Armand, J. M. Chabagno and P. Rigaud, *Solid State Ionics* **11**, 91 (1983).
12. M. Mali, J. Roos and D. Brinkmann: in K.A. Muller, R. Kind and J. Roos, editors. *Proceedings of XXII<sup>nd</sup> Congress Ampere*, University of Zurich, 1984.
13. S. Battacharja, S.W. Smoot and D.H. Whitmore, *Solid State Ionics* **18/19**, 306 (1986).

14. P.G. Bruce, in Reference 2, vol.1, p.237.
15. N. Boden, S.A. Leng and I.M. Ward, *Solid State Ionics* 45, 261 (1991).
16. K.J. Adamic, S.G. Greenbaum, K.M. Abraham, M. Alamgir, M.C. Wintersgill and J.J. Fontanella, *Chemistry of Materials* 3, 534 (1991).
17. M.C. Wintersgill, J.J. Fontanella, Y.S. Pak, S.G. Greenbaum, A. Al-Mударis and A.V. Chadwick, *Polymer* 30, 1123 (1989).
18. S.G. Greenbaum, Y.S. Pak, M.C. Wintersgill and J.J. Fontanella, *Solid State Ionics* 31, 241 (1988).
19. S.G. Greenbaum, Y.S. Pak, K.J. Adamic, M.C. Wintersgill, J.J. Fontanella, D.A. Beam, H.L. Mei and Y. Okamoto, *Molecular Crystals and Liquid Crystals* 160, 347 (1988).
20. (a) A. Baram, Z. Luz and S. Alexander, *Journal of Chemical Physics* 58, 4558 (1973). (b) A. Vega, unpublished work (presented at the Bat-Sheva Workshop on New Developments and Applications in ESR and NMR Spectroscopy, Israel, 1990).
21. Y.S. Pak, K.J. Adamic, S.G. Greenbaum, M.C. Wintersgill, J.J. Fontanella and C.S. Coughlin, *Solid State Ionics* 45, 277 (1991).
22. R.E. Stark, Y.S. Pak and S.G. Greenbaum, *ibid.* 34, 275 (1989).
23. S.G. Greenbaum, K.J. Adamic, Y.S. Pak, M.C. Wintersgill, J.J. Fontanella, D.A. Beam and C.G. Andeen, in: H. Tuller, editor. Proceedings of the Electrochemical Society Symposium on Electro-Ceramics and Solid State Ionics, Honolulu, 1987, vol. 88-3, Electrochemical Society, Pennington, NJ, 1987, p.211.
24. S. Panero, B. Scrosati and S.G. Greenbaum, *Electrochimica Acta*, in press.
25. S.H. Chung, K.R. Jeffrey and J.R. Stevens, *Journal of Chemical Physics* 94, 1803 (1991).
26. J.F. O'Gara, G. Nazri and D.M. MacArthur, *Solid State Ionics* 47, 87 (1991).
27. M.A. Ratner and A. Nitzan, *Faraday Discussions of the Chemical Society* 88, 19 (1989).

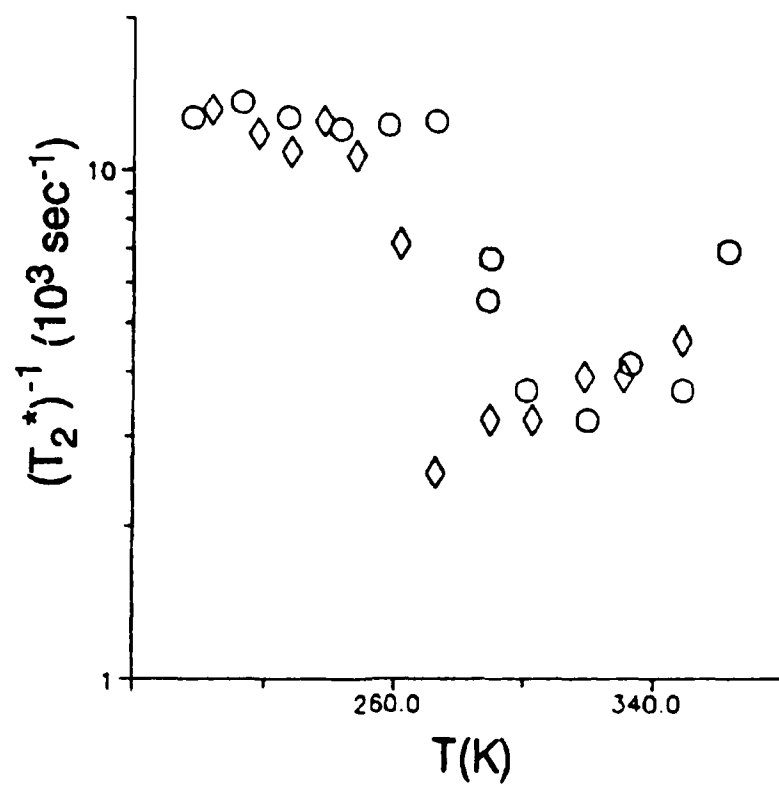
## FIGURE CAPTIONS

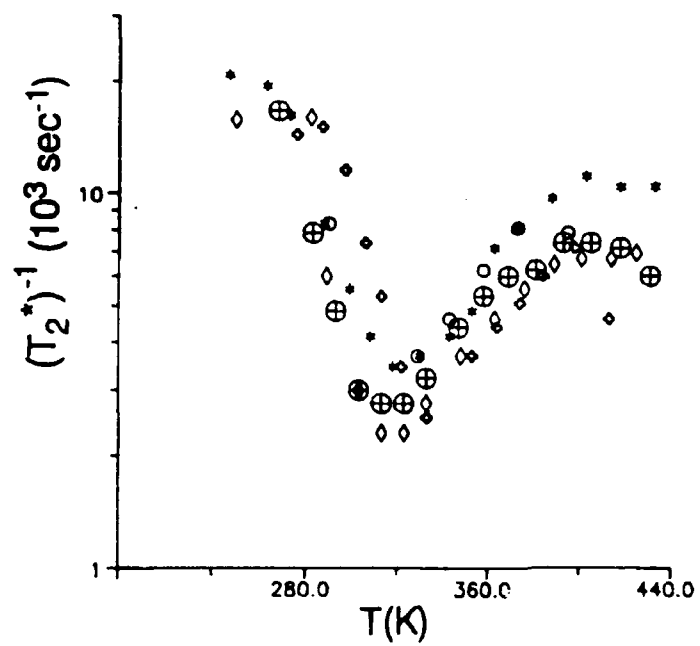
1. Arrhenius plot of  $^7\text{Li}$  NMR linewidths in MEEP/PEO or MEEP/PPO mixtures complexed with Li salts. The compositions of the samples are listed in the figure (from [16]).
2. Behavior of the linewidth (vertical axis) of the central transition in a spin-3/2 system (from [10(b)], adapted from [20]).
3. Reciprocal  $^{23}\text{Na}$  free induction decay constant  $T_2^*$ , which is proportional to the linewidth, in (a) oxymethylene-linked  $\text{PEO}_9\text{NaX}$ , where  $\text{X} = \text{CF}_3\text{SO}_3$  (diamonds) and  $\text{I}$  (circles). From [17]; (b)  $\text{PPO}_8\text{NaX}$ , where  $\text{X} = \text{I}$  (circles),  $\text{ClO}_4$  (crosses),  $\text{SCN}$  (stars),  $\text{CF}_3\text{SO}_3$  (diamonds) and  $(\text{CF}_3\text{SO}_3)_{0.5}(\text{I})_{0.5}$  (crosses inside circles). From [18]; (c) poly(monophenylsiloxane-co-ethylene oxide) complexed with  $\text{NaCF}_3\text{SO}_3$  (from [19]).
4. Two components of  $^{23}\text{Na}$  FID in  $\text{PPO}_8\text{NaI}$  at 329 K, corresponding to mobile ions (top) and immobile clusters (from [23]).
5. Full (top) and partially saturated  $^{23}\text{Na}$  spectra of  $\text{PPO}_8\text{NaClO}_4$  at 413 K. The saturated portion (left half of the top spectrum) corresponds to precipitated salt.
6. Full (top) and partially saturated  $^7\text{Li}$  spectra of MEEP/PPO: $\text{LiClO}_4$  (from [16], composition of sample given in fig.1).
7.  $^7\text{Li}$  spectra in  $\text{PEG}_9\text{LiBF}_4$  at  $\sim 200$  K. (a) full spectrum; (b) proton decoupled; (c)  $^{19}\text{F}$  decoupled.

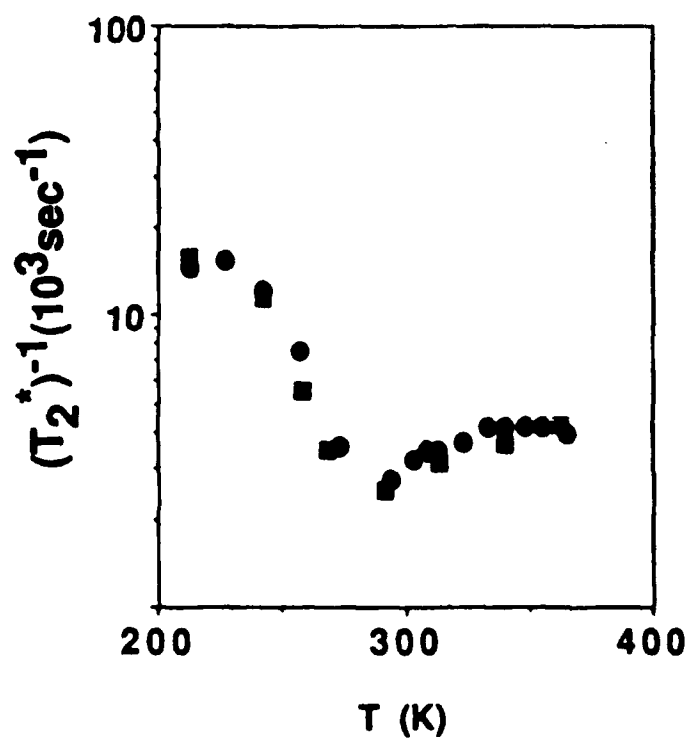


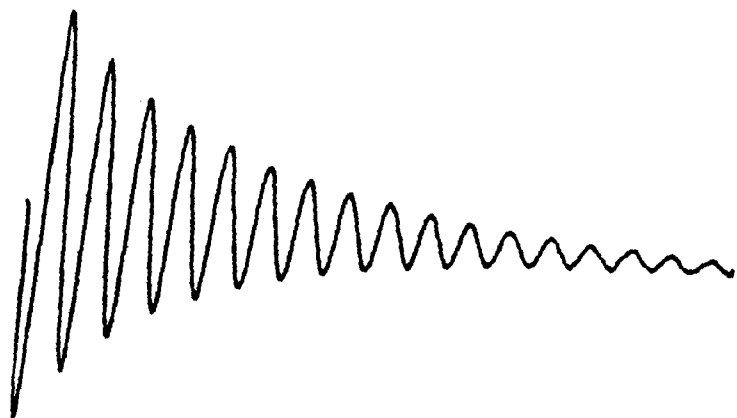




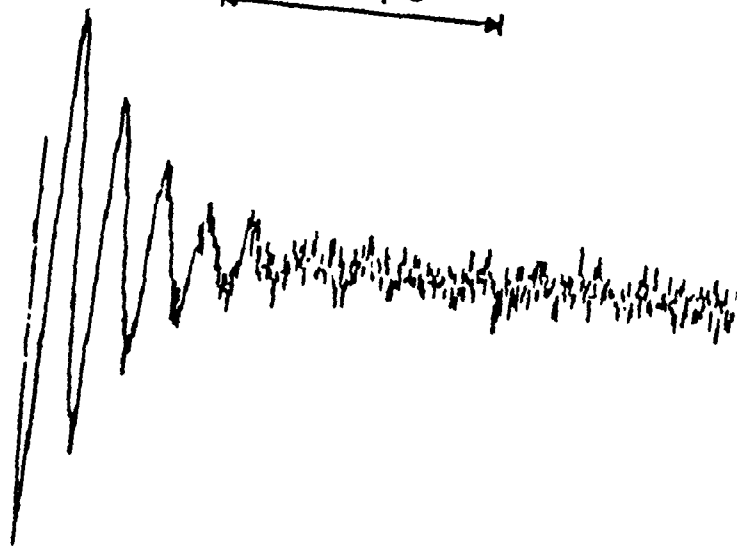


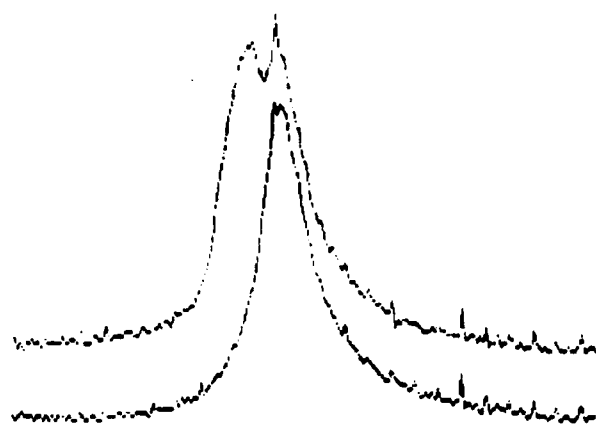






400  $\mu$ s





↔

5 kHz

**SAMPLE  
#5**

$T = 90^{\circ}\text{C}$

